

3. AIR ALGORITHMS

In this chapter the algorithms for the transport of chemical species within and among air compartments and diffusion/volatilization between air compartments and surface water are presented. A description of deposition from air compartments to surface water can be found in Chapter 4 and a description of the transport processes between the air compartments and soil can be found in Chapter 5. The text box on the next page provides a quick summary of the algorithms developed in this chapter and provides a definition of all parameters used.

3.1 AIR TO AIR ALGORITHMS

For a given wind speed and direction, there are two types of transfer considered from one air compartment to another:

- Advective transfer (bulk) due to the component of the wind vector normal to the boundary between the compartments; and
- Dispersive transfer (bulk) calculated from the component of the wind vector parallel to the boundary between the compartments.

The total transfer factor from one compartment to the other is the sum of these two transfer coefficients.

Let A_R and A_S denote the receiving and sending air compartments. If the boundary between the two air compartments is composed of n distinct line segments, then the transfer factor from the sending to the receiving air compartment is calculated as

$$T_{A_S \rightarrow A_R} = \frac{1}{V_S} \sum_{i=1}^n Area_i (u_i^{(D)} + u_i^{(L)}) \quad (3-1)$$

where:

V_S	=	volume of the sending air compartment (m ³)
$Area_i$	=	interfacial area across i th boundary (m ²)
$u_i^{(D)}$	=	direct advective wind velocity across the i th boundary (m/day)
$u_i^{(L)}$	=	lateral/dispersive wind velocity across the i th boundary (m/day)

Summary of Transport Algorithms Developed in this Chapter

Air compartment to air compartment:

$$T_{A_S \rightarrow A_R} = \frac{1}{V_S} \sum_{i=1}^n Area_i (u_i^{(D)})$$

Diffusion/volatilization from air compartment to surface water compartment:

$$T_{air \rightarrow water} = \frac{A}{V_a} K_v \frac{f_a(vapor)}{H/RT_k}$$

Diffusion/volatilization from surface water compartment to air compartment:

$$T_{water \rightarrow air} = \frac{A}{V_w} K_v f_w(liquid)$$

where:

V_S	=	volume of the sending air compartment (m ³)
$Area_i$	=	interfacial area across <i>i</i> th boundary (m ²)
$u_i^{(D)}$	=	direct advective wind velocity across the <i>i</i> th boundary (m/time)
A	=	interfacial area between the surface water and air compartments (m ²)
$f_w(liquid)$	=	fraction of chemical in the water compartment that is dissolved (unitless)
V_w	=	volume of water compartment (m ³)
$f_a(vapor)$	=	fraction of chemical in the air compartment that is in the vapor phase (unitless)
V_a	=	volume of air compartment (m ³)
K_v	=	volatilization transfer rate, m/day
R	=	universal gas constant (8.206x10 ⁻⁵ atm-m ³ /mole °K)
T_K	=	water temperature (°K)
H	=	Henry's law coefficient for the air-water partitioning of the chemical (atm-m ³ /mole)

3.1.1 Direct Advective Transfer

The direct wind flow across an air compartment boundary (notation $u^{(D)}$ is used above) is calculated by finding the projection of the wind vector onto the normal vector to the boundary between the air compartments.

Let $P_1=(x_1,y_1)$ and $P_2=(x_2,y_2)$ be the points defining the line that is the projection of the boundary onto the xy -plane (*i.e.*, the view from above of the vertical plane defining the boundary). It is assumed that the points P_1 and P_2 are ordered so that the receiving compartment is on the right side of the directed line segment starting at P_1 and ending at P_2 . The unit vector \vec{v} perpendicular to this line segment that is in the direction of the receiving compartment is given by:

$$\vec{v} = \frac{1}{\sqrt{(y_2-y_1)^2+(x_2-x_1)^2}} \langle y_2-y_1, -(x_2-x_1) \rangle = \langle \sin\phi, \cos\phi \rangle \quad (3-2)$$

where ϕ is the angle measured clockwise from due north. If the wind is blowing with speed u towards the direction ϑ (measured clockwise from due north), then the wind vector, denoted by \vec{w} , can be written:

$$\begin{aligned} \vec{w} &= \langle u \cos(\pi/2-\vartheta), u \sin(\pi/2-\vartheta) \rangle \\ &= u \langle \sin\vartheta, \cos\vartheta \rangle \end{aligned} \quad (3-3)$$

The projection of the wind vector \vec{w} onto \vec{v} is just the dot product $\vec{w} \cdot \vec{v}$ of the two vectors, which is given by:

$$\begin{aligned} \vec{w} \cdot \vec{v} &= \frac{u}{\sqrt{(y_2-y_1)^2+(x_2-x_1)^2}} [(y_2-y_1) \sin\vartheta - (x_2-x_1) \cos\vartheta] \\ &= u [\sin\vartheta \sin\phi + \cos\vartheta \cos\phi] \\ &= u \cos(\vartheta-\phi) \end{aligned} \quad (3-4)$$

Since \vec{v} is a unit vector, the dot product in this case is the component of the vector \vec{w} in the direction of \vec{v} . The wind flow rate from the sending compartment to the receiving compartment is defined to be the dot product if it is positive, otherwise it is zero; *i.e.*,

$$\text{Wind speed perpendicular to compartment boundary} = u_{\perp} = \max\{0, u \cos(\vartheta-\phi)\} \quad (3-5)$$

If the wind is blowing perpendicular to the boundary (*i.e.*, $\phi = 0$), then the wind flow rate across the boundary is just the wind speed; otherwise it is flowing with a velocity less than the wind speed, the magnitude of which depends on the difference in the angles of the wind speed and the boundary.

3.2 AIR TO SOIL ALGORITHMS

The algorithms describing the transfer of chemical mass between air and soil are presented in Section 5.4.3.

3.3 AIR TO SURFACE WATER ALGORITHMS

3.3.1 DEPOSITION

The algorithms describing the deposition of chemical mass from air to surface water are presented in Section 4.2.1.

3.3.2 DIFFUSION

3.3.2.1 Volatilization Transfer Between Surface Water and Air

The following describes the method used for estimating volatilization transfer between air and surface water for any chemical that has a nonzero Henry's law constant. The method is a two-layer resistance model first presented by Whitman (1923) and incorporated into the U.S. EPA WASP water quality model (Ambrose 1995). The proceeding discussion is based primarily on the WASP model documentation.

Volatilization is the movement of chemical across the air-water interface as the dissolved neutral concentration attempts to equilibrate with the gas phase concentration. Equilibrium occurs when the partial pressure exerted by the chemical in solution equals the partial pressure of the chemical in the overlying atmosphere. The rate of exchange is proportional to the gradient between the dissolved concentration and the concentration in air.

With the approach described in Whitman (1923), the dissolved concentration in the surface water is assumed to attempt to equilibrate with the gas phase concentration in the atmosphere, via the general equation:

$$\left(\frac{\partial C_{dissolved}}{\partial t} \right)_{volat} = \frac{K_v}{D} (C_{dissolved} - C_a / (H/RT_K)) \quad (3-6)$$

where:

$C_{dissolved}$	=	dissolved concentration of chemical (mass [chemical]/volume[water])
C_a	=	vapor phase concentration of chemical in air (mass [chemical]/volume [air])
K_v	=	volatilization transfer rate (m/day)
D	=	water depth (m)
R	=	universal gas constant (8.206x10 ⁻⁵ atm-m ³ /mole °K)
T_K	=	water temperature (°K)
H	=	Henry's law coefficient for the air-water partitioning of the chemical (atm-m ³ /mole).

The transfer rate can range from near 0 to 25 m/day, depending on conditions (Ambrose 1995). Multiplying the above equation by the volume of the water compartment, denoted here by V_w , yields:

$$Net\ Flux\ air\ to\ water\ (mass[chemical]/time) = V_w \frac{K_v}{D} (C_{dissolved} - C_a/(H/RT_K)) \quad (3-7)$$

The term V_w/D will be equal to the area of the water compartment, if the depth of the water compartment is approximately constant. This area is also the interfacial area between the air and water compartments, and so that:

$$Net\ Flux\ air\ to\ water = A K_v \left(f_w(liquid) \frac{N_w}{V_w} - f_a(vapor) \frac{N_a}{V_a} / (H/RT_K) \right) \quad (3-8)$$

or, using the notation of transfer factors,

$$T_{air \rightarrow water}(diffusion/volatilization) = \frac{A}{V_a} K_v \frac{f_a(vapor)}{(H/RT_K)} \quad (3-9)$$

$$T_{water \rightarrow air}(diffusion/volatilization) = \frac{A}{V_w} K_v f_w(liquid) \quad (3-10)$$

where:

A	=	interfacial area between the surface water and air compartments (m ²)
$f_w(liquid)$	=	fraction of chemical in the water compartment that is dissolved (unitless)
N_w	=	total mass of chemical in the water compartment (g)

V_w	=	volume of water compartment (m ³)
$f_a(vapor)$	=	fraction of chemical in the air compartment that is in the vapor phase (unitless)
N_a	=	total mass of chemical in the air compartment (g)
V_a	=	volume of air compartment (m ³)
K_v	=	volatilization transfer rate (m/day) [see below for details]
R	=	universal gas constant (8.206x10 ⁻⁵ atm-m ³ /mole °K)
T_K	=	water temperature (°K)
H	=	Henry's law coefficient for the air-water partitioning of the chemical (atm-m ³ /mole).

The two-resistance method assumes that two "stagnant films" are bounded on either side by well mixed compartments. Concentration differences serve as the driving force for the water layer diffusion. Pressure differences drive the diffusion for the air layer. From mass balance considerations, it is obvious that the same mass must pass through both films, thus the two resistances combine in series, so that the conductivity is the reciprocal of the total resistance:

$$K_v = (R_L + R_G)^{-1} = \left[K_L^{-1} + \left(K_G \frac{H}{RT_K} \right)^{-1} \right]^{-1} \quad (3-11)$$

where:

R_L	=	liquid phase resistance, day/m
K_L	=	liquid phase transfer coefficient, m/day
R_G	=	gas phase resistance, day/m
K_G	=	gas phase transfer coefficient, m/day.

There is actually yet another resistance involved, the transport resistance between the two interfaces, but it is assumed to be negligible (this may not be true in two cases: very turbulent conditions and in the presence of surface active contaminants).

The value of K_v , the conductivity, depends on the intensity of turbulence in a water body and in the overlying atmosphere. Mackay and Leinonen (1975) have discussed conditions under which the value of K_v is primarily determined by the intensity of turbulence in the water. As the Henry's Law coefficient increases, the conductivity tends to be increasingly influenced by the intensity of turbulence in water. As the Henry's Law coefficient decreases, the value of the conductivity tends to be increasingly influenced by the intensity of atmospheric turbulence.

Because Henry's Law coefficient generally increases with increasing vapor pressure of a compound and generally decreases with increasing solubility of a compound, highly volatile low solubility compounds are most likely to exhibit mass transfer limitations in water and relatively nonvolatile high solubility compounds are more likely to exhibit mass transfer limitations in the

air. Volatilization is usually of relatively less magnitude in lakes and reservoirs than in rivers and streams.

In cases where it is likely that the volatilization rate is regulated by turbulence level in the water phase, estimates of volatilization can be obtained from results of laboratory experiments. As discussed by Mill et al. (1982), small flasks containing a solution of a pesticide dissolved in water that have been stripped of oxygen can be shaken for specified periods of time. The amount of pollutant lost and oxygen gained through volatilization can be measured and the ratio of conductivities (KVOG) for pollutants and oxygen can be calculated. As shown by Tsivoglou and Wallace (1972), this ratio should be constant irrespective of the turbulence in a water body. Thus, if the reaeration coefficient for a receiving water body is known or can be estimated and the ratio of the conductivity for the pollutant to reaeration coefficient has been measured, the pollutant conductivity can be estimated.

The input computed volatilization rate constant is for a temperature of 20°C. It is adjusted for segment temperature using the equation:

$$K_{v,T} = K_{20} \Theta_v^{T-20} \quad (3-12)$$

where:

K_{20} = calculated volatilization transfer rate (m/day)
 Θ_v = temperature correction factor
 T = water temperature (°C).

3.3.2.2 Calculation of Volatilization Transfer Rates for the Whitman Two-Resistance Model

There are a variety of options available for how the transfer rates K_G and K_L are obtained, each of which will be implemented in TRIM.FaTE. These options are summarized in Tables 3-1 and 3-2.

Table 3-1
Methods for Determining Gas Phase Transfer Coefficient K_G^a for the Whitman Two-Resistance Volatilization Model Between Air and Surface Water

	Method	K_G , Gas phase transfer coefficient (m/day)	Reference/Comment
Stagnant Pond or Lake	1.	$K_G = u^* (\kappa^{0.33} / \lambda_2) Sc_a^{-0.67}$ where: u^* = the shear velocity (m/s) computed from $u^* = C_d^{0.5} W_{10}$ where: C_d = drag coefficient (0.0011) W_{10} = wind velocity 10 m above water surface (m/sec) κ = von Karmen's constant (0.74) λ_2 = dimensionless viscous sublayer thickness (4) where Sc_a and Sc_w are air and water Schmidt Numbers, computed from $Sc_a = \frac{\mu_a}{\rho_a D_a}$ $Sc_w = \frac{\mu_w}{\rho_w D_w}$ D_a = diffusivity of chemical in air (m ² /sec), = $1.9E-4 / M_w^{2/3}$ D_w = diffusivity of chemical in water (m ² /sec) = $22E-9 / M_w^{2/3}$ μ_a = viscosity of air, internally calculated from air temperature, kg/m-sec = $(1.32 + 0.009 T_{ac})/10$, T_{ac} =air temperature (C) μ_w = viscosity of water, internally calculated from water temperature, kg/m-sec = $10^{(-3.0233 + 1301/(998.333+8.1855(T_w-20) + 0.00585 8.1855(T_w-20)^2))}$, T_w =water temperature (C) M_w = molecular weight of compound	O'Connor (1983), Ambrose (1995)
Stagnant Pond or Lake	2.	See Method (1) for definition of terms. $K_G = 10^{-3} + 0.0462 u^* Sc_a^{-0.67}$	Mackay and Yeun (1983), Ambrose (1995)
Flowing stream, River, or Estuary	1.	Same as Method (1) for stagnant water body.	
Flowing stream, River, or Estuary	2.	Same as Method (2) for stagnant water body.	
Flowing stream, River, or Estuary	3.	Input value of 100 m/day	Ambrose (1995)

^a Used in the calculation of the volatilization transfer rate K_v : $K_v = (R_L + R_G)^{-1} = \left[K_L^{-1} + \left(K_G \frac{H}{RT_K} \right)^{-1} \right]^{-1}$

Table 3-2
Methods for Determining Liquid Phase Transfer Coefficient K_L ^a for the Whitman Two-Resistance Volatilization Model
Between Air and Surface Water

	Method	K_L , Liquid phase transfer coefficient (m/day)	Reference/Comment
Stagnant Pond or Lake	1.	$K_a * K_{vo}$, where K_a =input=reaeration velocity (m/day) K_{vo} =input=ratio of volatilization rate to reaeration rate	Ambrose (1995)
Stagnant Pond or Lake	2.	$K_a * (32/M_w)^{0.5}$, where K_a =input=reaeration velocity (m/day) M_w =molecular weight of chemical (g/mole)	Ambrose (1995)
Stagnant Pond or Lake	3.	$K_L = u^* (\rho_a / \rho_w)^{0.5} (\kappa^{0.33} / \lambda_2) Sc_w^{-0.67}$ <p>where: u^* = the shear velocity (m/s) computed from $u^* = C_d^{0.5} W_{10}$ where: C_d = drag coefficient (0.0011) W_{10} = wind velocity 10 m above water surface (m/sec) ρ_a = density of air, internally calculated from air temperature (kg/m³) ρ_w = density of water, internally calculated from water temperature (kg/m³) κ = von Karmen's constant (0.74) λ_2 = dimensionless viscous sublayer thickness (4) Sc_a and Sc_w are air and water Schmidt Numbers, computed from</p> $Sc_a = \frac{\mu_a}{\rho_a D_a} \qquad Sc_w = \frac{\mu_w}{\rho_w D_w}$ <p>where: D_a = diffusivity of chemical in air (m²/sec), = $1.9E-4 / M_w^{2/3}$ D_w = diffusivity of chemical in water (m²/sec) = $22E-9 / M_w^{2/3}$ μ_a = viscosity of air, internally calculated from air temperature (kg/m-sec) = $(1.32 + 0.009 T_{ac})/10$, T_{ac}=air temperature (C) μ_w = viscosity of water, internally calculated from water temperature (kg/m-sec) = $10^{(-3.0233 + 1301/(998.333+8.1855(T_w-20) + 0.00585 8.1855(T_w-20)^2))}$, T_w=water temperature (C)</p>	O'Connor (1983), Ambrose (1995)

Table 3-2 (continued)
Methods for Determining Liquid Phase Transfer Coefficient K_L for the Whitman Two-Resistance Volatilization Model Between Air and Surface Water

	Method	K_L , Liquid phase transfer coefficient (m/day)	Reference/Comment
Stagnant Pond or Lake	4.	$K_L = \begin{cases} 10^{-6} + 0.00341 u^* S_{cw}^{-0.5} & \text{if } u^* > .3 \text{ m/s} \\ 10^{-6} + 0.0144 u^{*0.22} S_{cw}^{-0.5} & \text{if } u^* < .3 \text{ m/s} \end{cases}$ <p>See Method (4) for definition of terms.</p>	Mackay and Yeun (1983), Ambrose (1995)
Flowing stream, River, or Estuary	1.	Same as Method (1) for stagnant water body.	
Flowing stream, River, or Estuary	2.	Same as Method (2) for stagnant water body.	
Flowing stream, River, or Estuary	3.	Same as Method (3) for stagnant water body.	
Flowing stream, River, or Estuary	4.	$K_L = \begin{cases} K_a K_{vo}, \text{ where } K_a = 5.349 \frac{u^{0.67}}{D^{0.85}}, K_{vo} = \text{input or } \sqrt{32/M_w} & \text{if } D < 0.61 \text{ m} \\ (D_w u/D)^{0.5} 8.64 \times 10^4 & \text{if } D \geq 0.61 \text{ m and } (u < 0.518 \text{ m/s or } D > 13.584 u^{0.29135}) \\ 5.049 \frac{u^{0.969}}{D^{0.673}} & \text{else} \end{cases}$ <p>where: u = velocity of water (m/s) D = water compartment depth (m) D_w = diffusivity of chemical in water (m²/sec) $= 22\text{E-}9 / M_w^{2/3}$</p>	Covar (1976), Ambrose (1995)

^a Used in the calculation of the volatilization transfer rate K_v :
$$K_v = (R_L + R_G)^{-1} = \left[K_L^{-1} + \left(K_G \frac{H}{RT_K} \right)^{-1} \right]^{-1}$$